STIMULI-RESPONSIVE PERIODIC MICRO STRUCTURES ON OXIDE-POLYMER HYBRID FILMS

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Fabrication of smart responsive materials by multiscale composites with hierarchical structures is one of the current trends in materials science[1].We have reported that hybrid organic-inorganic films consisted of titania precusor, a viscosity-controlling agent (poyvinylpyrrolidone, PVP) and a polymerizable monomer (acrylamide, AM) form wrinkled microstructures with a long range order upon illumination by UV light. The fast polymerization of AM at the film-air interface produces a wrinkling effect that is used to obtain micropatterned structures[2]. In this study we show an example of such type of materials whose responsive behavior to specific external stimuli is driven by a controlled combination of properties at nano and micron length scale.

We have followed the idea that if we could maintain the material into a "soft state" in a controlled way and introduce another phase that is able to respond to a specific external stimulus, we should finally obtain an example of hierarchical stimuli-responsive material. PVP was used as a plasticizer / swelling agent to attain the stimuli response. We have then exposed the hybrid NP-TiO_2-CTAB-PVP-AM films to UV light to induce formation of wrinkled microstructures with a well-defined long-range periodicity of around 15 μm. **Fig. 1** shows the optical image of the surface of a long-range ordered wrinkled film; the cross section optical micrograph indicates the formation of two layers that we attribute to a stiff poly-AM surface layer and a NP-TiO_2-CTAB -PVP hybrid gel under layer[3]. The wrinkling is produced as effect of preferential polymerization of AM at the surface induced by UV light; long-range ordered periodic structures could be achieved because of the anisotropic stress raised at the edges of the substrate after the illumination [4]. Stress accumulation along with the gelation of the TiO_2-CTAB -PVP layer is only limited to the direction parallel to the substrate edge. Therefore, we have obtained long-range ordered periodic structures without any external intervention.

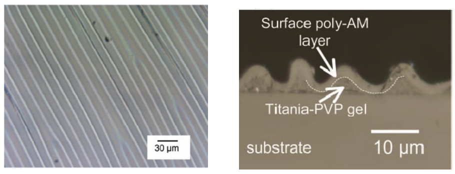

Fig. 1 Optical microscopy image of (left) surface wrinkles with a long range order and (right) cross-sectional image of the cracked substrate, in which the interface between surface poly-AM and titania-PVP gel layers is shown by a dotted line as guide for the eye

We have exposed these films with long-range ordered wrinkles to an external stimulus, such as a change in relative humidity in the atmosphere; a fast recover of the wrinkles with the formation of a smooth transparent surface has been observed. This macroscopic change is illustrated in **Fig. 2**, which shows the wrinkled film (left image) that transforms into a smooth surface (right image) in a 100% RH environment. This response to RH is reversible and several cycles can be performed (we have observed a reversible effect up to 50 cycles).

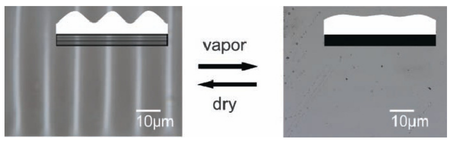

Fig 2. Optical microscopy images of long-range ordered surface wrinkles before (left image) and after water vapor treatment (right image). In the insets, a sketch of the surface change during the process is depicted.

We have tested the capability of the material to response to cyclic stimuli performing in-situ measurements by small-angle light scattering (SALS) at different RH conditions. When the samples show wrinkles on the surface, as we have seen, they act as "Bragg gratings" by diffracting the He-Ne laser light because of the regular spacing between wrinkles[5]; the more is the surface corrugation, the higher diffraction efficiency is attained. To measure the change of the first order diffraction efficiency ((intensity of the first order diffraction spots) / (intensity of the incident laser light)) along with the surrounding humidity, the films were put in an atmosphere-controlled chamber. The diffraction efficiency of the first order diffraction spots as a function of the RH in the chamber was measured by an optical power meter. **Fig. 3** shows the change of diffraction efficiency measured by in-situ SALS in dry-wet cycles: when the film is wrinkled the diffraction efficiency increases, whereas in wet conditions, the film surface becomes smoother and this efficiency drops. If we compare these variith the changes in RH, we observe that there is a sigmoidal correlation between the change of the surface and that of the external atmosphere humidity.

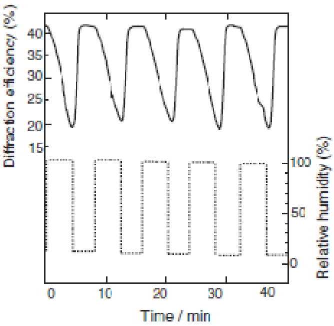

Fig. 3 Humidity response in a wet(3 min) – dry(5 min) cycle of long-range ordered surface wrinkles measured by a change in diffraction effi ciency of the 1st-order diffraction spots of a He-Ne laser light

This simple and efficient response of the material is due to its hierarchical nature: the laser light diffraction properties are strictly correlated to the micron-scale self-organization but the stimuli-responsive capability is controlled by the material structure at the nano-scale. These results show that the material has a very peculiar structural property; immediately after the deposition, the film is in a "wet state" and wrinkling can be induced by formation of a harder poly-AM surface layer by UV light (**Fig.1**). However, the material even after wrinkling is still in a "soft" state, the titania nanostructures and organic polymers drive the responsive behavior. The material is still able to change physical state (**Fig. 4, left image**) and this change is caused by the hydrophilic PVP [6] which swells by absorbing water and attains the plastic deformation for smoothing the surface of the "soft" wrinkling film (**Fig. 4**, right image). We have systematically checked the role of each component of this multi-scale material: without titania, wrinkling is not observed at all, while without CTAB the RH response of the material is not reproducible.

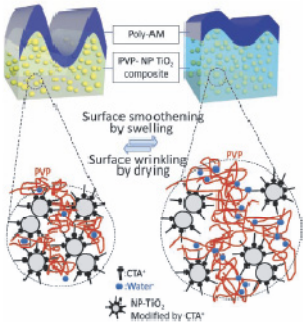

Fig. 4 Idealized images of the wrinkling – smoothing process in the titania-hybrid films. The photopolymerization process produces wrinkles (left image). The PVP phase in the PVP-NP TiO_2 composite absorbs water upon exposure to a wet atmosphere so that the wrinkles in the film disappear as an effect of swelling (right image)

In conclusion photo-fabrication of titania based hybrid organic-inorganic composite films allows preparing tunable hierarchical structures with environment-responsive properties. The material is formed by a hybrid organic-inorganic structure which contains NP-TiO_2 stabilized with an ionic surfactant and PVP as plasticizer. After exposing the film to UV-light, wrinkles are spontaneously formed, which are indeed responsive to external stimuli. Changing the relative humidity, the film swells by absorbing water and in turn the wrinkles are smoothed; this response is reversible and wet-dry cycles can be run.

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